

# Bound states of negatively charged ions induced by a magnetic field

Victor G. Bezhastnov, Peter Schmelcher, and Lorenz S. Cederbaum

*Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, INF 229, D-69120 Heidelberg,  
Federal Republic of Germany*

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We analyse the bound states of negatively charged ions which were predicted to exist because of the presence of a magnetic field by Avron *et al* [1]. We confirm that the number of such states is infinite in the approximation of an infinitely heavy nucleus and provide insight into the underlying physical picture by means of a combined adiabatic and perturbation theoretical approach. We also calculate the corresponding binding energies which are qualitatively different for the states with vanishing and non-vanishing angular momentum. An outlook on the case of including center of mass effects is presented.

## I. INTRODUCTION

The behaviour and properties of negative ions became during the past years a branch of intense research. There exists an enormous interest in the electronic structure and dynamics of negative ions, both from the theoretical as well as experimental point of view (see, e.g., the review [2] and the references therein). According to our present knowledge about atomic ions it is most likely that singly charged negative ions possess in the absence of a magnetic field only one stable ground-state configuration. For example for the  $H^-$  ion, this state is the  $1^1S$  electronic state, and a rigorous proof that this is the only possible bound state was given in [3]. Also, some atoms, like for example Be, N, Ne, Mg, Ar do not possess any stable negative ion state (see, e.g., [4,5]). On the other hand, one can expect that in the presence of a magnetic field a lot of new discrete energy states of negative ions can appear. This expectation is based on the statement that for any negatively charged ion the number of discrete energy states is infinite in the presence of a magnetic field [1]. However, this statement was formulated as the conclusion of a formal mathematical treatment which does not provide a transparent physical picture of the appearance of the infinite sequence of bound states nor does it estimate the corresponding energies. Although a wide set of works was focused on the influence of the magnetic field on low-lying ion states (e.g., [6–12]), there is no systematic treatment of the highly excited anions predicted in [1]. In the present paper we develop a physical approach showing transparently from which quantum mechanical grounds the infinite sequence of bound anion states appears in the presence of a magnetic field. In Section 2, we first reduce the problem to a one-particle, and then to a one-dimensional one, where to analyse the bonding one has to consider the motion of the external electron along the magnetic field in an effective potential depending on the quantum state. We confirm that, in the approximation of the static (infinitely heavy) nucleus, the number of the bound states is infinite, and derive estimates for the corresponding binding energies valid for arbitrary ions. In Section 3, we apply these estimates to the ion  $H^-$  and verify them treating the one-dimensional motion of the external electron numerically. We also discuss the bound states of an exotic ion formed by attaching the muon to the hydrogen atom. Besides, we analyse the importance of the non-adiabatic coupling between the states of the external and atomic (core) electrons. A general discussion and concluding remarks are given in Section 4.

## II. GENERAL

It is well-known (see, e.g., [4,13]) that the electron affinities for the negative ions are usually much smaller than the binding energies of the corresponding neutrals. This fact implies that the extra electron is weakly bound to the atom and its behaviour and properties strongly differ from that of internal (core) electrons. For the  $H^-$ -ion, the binding of the extra electron is exclusively due to correlation between the two electrons. In the following we will study the highly excited states of the negative ions which appear in the presence of a magnetic field and which, as we will estimate, correspond to very small electron affinities. We therefore use the approximation of a weakly bound external electron neglecting its exchange interaction with the core electrons. To exploit such a model, it is convenient to split the total Hamiltonian for a singly negatively charged ion into three terms,

$$H_{\text{ion}} = H_{\text{at}} + H_e + W. \quad (1)$$

Here the first term,

$$H_{\text{at}} = \frac{1}{2m_e} \sum_{a=1}^Z \left[ \mathbf{p}_a + \frac{e}{c} \mathbf{A}_a \right]^2 + U + 2\mu_B \mathbf{B} \boldsymbol{\Sigma} \quad (2)$$

describes a neutral atom with infinitely heavy nucleus in a magnetic field  $\mathbf{B}$  with the vector potential  $\mathbf{A}_a = \mathbf{A}(\mathbf{r}_a)$ . Summation is carried out over all the atomic (core) electrons labelled with the subscript “ $a$ ”,  $Z$  is the nucleus charge number,  $m_e$  and  $-e = -|e| < 0$  are the electron mass and charge. The potential energy  $U$  includes the Coulomb energies of the interaction of the core electrons with each other and with the nucleus.  $\boldsymbol{\Sigma}$  is the total spin of the atom, and  $\mu_B = e\hbar/(2m_e c)$  is the Bohr magneton. The second term in (1),

$$H_e = \frac{1}{2m_e} \left[ \mathbf{p} + \frac{e}{c} \mathbf{A} \right]^2 + 2\mu_B \mathbf{B} \boldsymbol{\sigma}, \quad (3)$$

corresponds to an extra (with respect to the atom) electron,  $\boldsymbol{\sigma}$  is the electron spin. The last term,

$$W = \sum_{a=1}^Z \frac{e^2}{|\mathbf{r} - \mathbf{r}_a|} - \frac{Ze^2}{r}, \quad (4)$$

describes the Coulomb coupling of the extra electron to the atom.

When the extra electron is weakly bound to the atom, the character of its motion differs strongly from that of the core electrons. In particular, the external electron can be assumed to move much slower than the core ones. In this case, the ion states can be successfully described in terms of a quasimolecular approach, and the problem of binding can even be reduced to a one-particle one. Below we briefly describe this approach.

### A. Quasimolecular approach to the problem of binding

Let us consider the Hamiltonian

$$H'_{\text{at}} = H_{\text{at}} + W. \quad (5)$$

It does not include the kinetic energy of the external electron, therefore the latter can be considered as static in space, so  $H'_{\text{at}}$  describes the motion of the core electrons only. Since the potential energy term

of  $H'_{\text{at}}$  depends parametrically on the position  $\mathbf{r}$  of the external electron, the energy spectrum of this Hamiltonian as well as the corresponding eigenfunctions also depend on  $\mathbf{r}$ . Let us denote them by

$$E'_i(\mathbf{r}) = \langle i | H'_{\text{at}} | i \rangle \quad (6)$$

and  $\phi_i(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_Z; \mathbf{r})$ , respectively, where the index  $i$  labels the eigenstates of the Hamiltonian  $H'_{\text{at}}$  with some choice of  $\mathbf{r}$ . Since at any  $\mathbf{r}$  the states  $|i\rangle$  compose a complete basis set, an eigenfunction of the total Hamiltonian (1) can be presented as

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_Z; \mathbf{r}) = \sum_{i'} \psi_{i'}(\mathbf{r}) \phi_{i'}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_Z; \mathbf{r}), \quad (7)$$

with the expansion coefficients  $\psi_{i'}(\mathbf{r})$  depending on the position of the external electron. It should be noted that this wave function is not completely antisymmetric with respect to all the ion electrons, only its “atomic part”,  $\phi_{i'}$  can be assumed to be properly antisymmetric with respect to the core electrons. Complete antisymmetrisation would significantly complicate the further consideration. On the other hand, the main yield of such a complication would be taking into account exchange interaction between the external and core electrons which is definitely negligible for states for which the external electron is localized far from the atom. Notice also that the form (7) of the ion wave function is exact if another charged particle different from the electron (like for example a muon) is attached to the atom.

Substituting the wave function (7) into the Schrödinger equation with the Hamiltonian (1), subsequently multiplying from the left-hand side by  $\phi_i^*$  and integrating over the positions of the core electrons we will arrive at the set of coupled equations

$$[H_e + E'_i(\mathbf{r}) + h_{ii}(\mathbf{r}) - E_{\text{tot}}] \psi_i(\mathbf{r}) = - \sum_{i' \neq i} h_{i'i'} \psi_{i'}(\mathbf{r}). \quad (8)$$

Here  $E_{\text{tot}}$  is the total eigenenergy of the system, and the matrix elements  $h_{i'i'}$  are given by the following equation

$$h_{i'i'} = \frac{1}{2m_e} \langle \phi_i^* | p^2 \phi_{i'} \rangle + \frac{e\mathbf{B}}{2m_e c} \langle \phi_i^* | \mathbf{l} \phi_{i'} \rangle + \frac{1}{m_e} \langle \phi_i^* | \mathbf{p} \phi_{i'} \rangle \mathbf{p}, \quad (9)$$

where  $\mathbf{l} = \mathbf{r} \times \mathbf{p}$  is the angular momentum of the external electron. Notice that if both  $i$  and  $i'$  relate to the ground state of the atom,  $|0\rangle$ , then the last two terms in Eq. (9) equal zero while the first term can be transformed as follows

$$h_{00} = \frac{\hbar^2}{2m_e} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \dots \int d\mathbf{r}_Z \left| \frac{\partial}{\partial \mathbf{r}} \phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_Z; \mathbf{r}) \right|^2. \quad (10)$$

In the following we restrict ourself by considering the attachment of the extra electron to the neutral atom in the ground state. In this case, the right-hand side of Eq. (8) is associated with the coupling between the ground and excited states of the core electrons due to the motion of the external electron. Assuming the ground state of the neutral atom to be energetically well-separated from the excited states this coupling can be neglected. Then Eq. (8) becomes essentially a one-particle Schrödinger equation,

$$[H_e + V_0(\mathbf{r}) + h_{00}(\mathbf{r}) - E_0] \psi_0(\mathbf{r}) = 0, \quad (11)$$

where, for the sake of convenience, we have shifted the energies by the ground state energy of the isolated atom,  $E_0^{(0)} = E'_0(r \rightarrow \infty)$ , and introduced

$$E_0 = E_{\text{tot}} - E_0^{(0)} \quad (12)$$

and

$$V_0(\mathbf{r}) = E'_0(\mathbf{r}) - E_0^{(0)}. \quad (13)$$

Equation (11) describes the motion of the external electron in the magnetic field and the potential which consists of two parts: the static term,  $V_0(\mathbf{r})$ , and the non-adiabatic (dynamic) correction,  $h_{00}(\mathbf{r})$ . The latter, as we shall directly estimate for the  $\text{H}^-$ -ion, decreases with increasing  $r$  faster than  $V(\mathbf{r})$  and can be neglected at distances exceeding the atomic size. Therefore, to analyse the binding mechanism for the excited ion states one has to solve the Schrödinger equation

$$[H_e + V(\mathbf{r}) - E] \psi(\mathbf{r}) = 0, \quad (14)$$

where for brevity we have omitted the index “0” related to the ground state of the core electrons.

At distances of the extra electron from the atom strongly exceeding the atom size, one can consider the operator (4) as a perturbation of the atom and evaluate it by the multipole expansion,

$$W = -e \left( \frac{\mathbf{D}\mathbf{n}}{r^2} - \frac{Q_{\alpha\beta} n_\alpha n_\beta}{2r^3} + \dots \right), \quad (15)$$

where  $\mathbf{n} = \mathbf{r}/r$  is the unit vector in the direction of  $\mathbf{r}$  and the indices  $\alpha$  and  $\beta$  run over the Cartesian coordinates.

$$\mathbf{D} = -e \sum_{a=1}^Z \mathbf{r}_a \quad (16)$$

and

$$Q_{\alpha\beta} = -e \sum_{a=1}^Z (r_a^2 \delta_{\alpha\beta} - 3x_{a\alpha} x_{a\beta}) \quad (17)$$

are the operators of the dipole and quadrupole momenta of the atom, respectively,  $x_{a\alpha}$  and  $x_{a\beta}$  denote the components of  $\mathbf{r}_a$ ,  $\mathbf{r}_a = (x_{a1}, x_{a2}, x_{a3})$ . Then the potential in Eq. (14) can be approximated as

$$V(\mathbf{r}) = -\frac{e\langle \mathbf{D} \rangle \mathbf{n}}{r^2} + \frac{e\langle Q_{\alpha\beta} \rangle n_\alpha n_\beta}{2r^3} - \frac{e^2 \kappa_{\alpha\beta} n_\alpha n_\beta}{2r^4}, \quad (18)$$

where  $\langle \mathbf{D} \rangle$  and  $\langle Q_{\alpha\beta} \rangle$  are the mean values of the dipole and quadrupole momenta, respectively, of the unperturbed atom described by the Hamiltonian (2), and  $\kappa_{\alpha\beta}$  is the polarizability of the atom in an electric field. The first two terms in (18) represent the first-order perturbation corrections. The last term in (18) is the second-order correction, it corresponds to the dipole term in (15) treated as the perturbation of the atom by the electric field  $\mathcal{E} = -en/r^2$ .

Expression (18) can be further simplified if we take into account that the potential (13) has its symmetry axes directed along the magnetic field. A simple argumentation of this statement is the following. In the presence of the magnetic field it is natural to assume that the axis of quantization for the atom is directed along  $\mathbf{B}$ . Then the potential (13) depends parametrically on the two vectors,  $\mathbf{B}$  and  $\mathbf{r}$ . Since the potential is scalar it must depend only on scalars which can be constructed from these vectors. These scalars are  $B^2$ ,  $r^2$  and  $\mathbf{Br}$ . This means that if  $\mathbf{B}$  is directed along the  $z$ -axes, then  $V(\mathbf{r}) = V(r_\perp, z)$ . As a result the non-zero components of the mean dipole and quadrupole momenta of the neutral atom can only be  $\langle D_z \rangle$ ,  $\langle Q_{xx} \rangle = \langle Q_{yy} \rangle$  and  $\langle Q_{zz} \rangle$ , respectively. Also, the polarizability takes the diagonal form with the components  $\kappa_{xx} = \kappa_{yy} = \kappa_\perp$  and  $\kappa_{zz} = \kappa_\parallel$ . Furthermore, since the  $z$ -parity of the core

electrons is the integral of motion when they are not perturbed by the interaction with the external electron, we have  $\langle D_z \rangle = 0$ . Then Eq. (18) can be transformed as follows:

$$V(r_{\perp}, z) = \frac{e^2 \lambda (2z^2 - r_{\perp}^2)}{2r^5} - (\kappa_{\perp} \sin^2 \vartheta + \kappa_{\parallel} \cos^2 \vartheta) \frac{e^2}{2r^4}, \quad (19)$$

where  $\vartheta$  is the angle between  $\mathbf{n}$  and  $\mathbf{B}$  and the coefficient  $\lambda$  can be expressed in terms of the mean values of the squares of the longitudinal and transverse coordinates of the core electrons of the unperturbed atom,

$$\lambda = \sum_{a=1}^Z [2\langle z_a^2 \rangle - \langle r_{a\perp}^2 \rangle]. \quad (20)$$

### B. Binding in a magnetic field as 1D problem

The Hamiltonian that determines the one-particle Schrödinger equation (14) explicitly reads

$$H_{\text{eff}} = \frac{p_z^2}{2m_e} + \frac{\pi_{\perp}^2}{2m_e} + V(r_{\perp}, z), \quad (21)$$

where

$$\pi_{\perp} = \mathbf{p}_{\perp} + \frac{e}{2c} \mathbf{B} \times \mathbf{r}_{\perp} \quad (22)$$

is the transverse kinetic momentum of the electron. We have introduced the symmetric gauge of the vector potential,  $\mathbf{A} = (1/2)\mathbf{B} \times \mathbf{r}$ , being the most appropriate one because of the axial symmetry of the potential  $V$ . We also have omitted the spin part of the Hamiltonian which determines the trivial shift of the ion energy spectrum and does not affect the binding energies.

Since the potential in the Hamiltonian (21) decreases rapidly with increasing distance of the extra electron from the atom, even quite a weak magnetic field can influence the transverse motion of the extra electron to a much larger extent than the atomic potential. In this case the eigenfunction of the Hamiltonian (21) can be efficiently expanded in terms of the Landau states,  $\langle \mathbf{r}_{\perp} | n, s \rangle$ , of the motion of the electron across the magnetic field. These states are the common eigenstates of the operators  $\pi_{\perp}^2$  and  $l_z$ , where  $\mathbf{l} = \mathbf{r} \times \mathbf{p}$  is the electron angular momentum, and labeled with the two quantum numbers,  $n$  and  $s$ , that determine the corresponding eigenvalues,

$$\begin{aligned} \pi_{\perp}^2 &= (\hbar/a_m)^2 (2n+1), \quad n = 0, 1, 2, \dots, \\ l_z &= -\hbar s, \quad s = -n, -n+1, -n+2, \dots, \end{aligned} \quad (23)$$

$a_m = \sqrt{c\hbar/(eB)}$  is the magnetic length. The first eigenvalue determines the Landau energy spectrum

$$E_n^{\text{Lan}} = \frac{\pi_{\perp}^2}{2m_e} = \frac{\hbar e B}{m_e c} \left( n + \frac{1}{2} \right). \quad (24)$$

Hence  $n$  is called the electron Landau level number.

Because of the axial symmetry of the atomic potential the longitudinal component of the electron angular momentum is an integral of motion for the Hamiltonian (21),  $[l_z, H_{\text{eff}}] = 0$ , and the quantum number  $s$  can be used to label the eigenstates of  $H_{\text{eff}}$ , i.e.  $E = E_s$ . The expansion of the corresponding eigenfunctions over the Landau states thus involves only different Landau level numbers and reads

$$\psi_s(\mathbf{r}) = \sum_n g_{ns}(z) \langle \mathbf{r}_\perp | n, s \rangle. \quad (25)$$

The expansion coefficients  $g_{ns}(z)$  and the energy  $E$  can be found by solving the system of coupled equations,

$$\left[ \frac{p_z^2}{2m_e} + V_{nn}^{(s)}(z) + E_n^{\text{Lan}} - E_s \right] g_{ns}(z) = - \sum_{n' \neq n} V_{nn'}^{(s)}(z) g_{n's}(z), \quad n = 0, 1, 2, \dots, \quad (26)$$

where

$$V_{nn'}^{(s)}(z) = \langle n, s | V(r_\perp, z) | n', s \rangle \quad (27)$$

are the effective longitudinal potentials obtained as the matrix elements of the atomic potential  $V(r_\perp, z)$  within the space of the Landau states of the external electron.

The quantity  $E_0^{\text{Lan}} = \hbar\omega_B/2$ , where  $\omega_B = eB/(m_e c)$  is the electron cyclotron frequency, determines the continuum threshold for the states of the external electron. The states of this electron belong to different manifolds associated with the different Landau energies  $E_n^{\text{Lan}}$ ,  $n = 0, 1, 2, \dots$ . The bound states can be classified by the numbers  $(s, n, \nu)$  where  $\nu$  equals the number of nodes of the function  $g_{ns}(z)$  for the leading term in the expansion (25) - such a classification is similar to that used in treating hydrogen-like atoms in a strong magnetic field, see, e.g., [14].

We can expect (and our results for the ion H<sup>-</sup> confirm this), that the binding energies for the ionic states induced by the presence of the magnetic field are small compared to the electron cyclotron energy,  $\hbar\omega_B$ . Therefore, all such states associated with the manifolds  $n = 1, 2, \dots$  lie in the continuum, i.e. are not bound. We thus will focus on the states related to the ground Landau manifold,  $n = 0$ . While treating them we can further neglect the coupling of the ground Landau manifold to the higher ones, e.g., omit the sum on the right-hand side of Eq. (26). This approach yields the 1D Schrödinger equation,

$$\left[ \frac{p_z^2}{2m_e} + V_s(z) - \varepsilon_s \right] g_s(z) = 0, \quad (28)$$

which describes the motion of the external electron along the magnetic field. In this equation, we have shifted the energy by the zero-point Landau energy,

$$\varepsilon_s = E_s - E_0^{\text{Lan}}. \quad (29)$$

Then, when  $\varepsilon_s$  is negative, the value of  $-\varepsilon_s$  is the binding energy of the external electron. Also, for brevity we have omitted the index  $n = 0$  and define the effective longitudinal potential by  $V_s(z) = V_{00}^{(s)}(z)$ . In order to get an idea of the binding properties of this potential one can use the weak coupling one-dimensional theory (see, e.g., [15]). This theory says that if the potential vanishes at  $|z| \rightarrow \infty$  and the integral

$$I_s = \int_{-\infty}^{\infty} V_s(z) dz \quad (30)$$

is negative than there is at least one bound state of finite longitudinal motion, and the estimate of the corresponding binding energy for that state is

$$-\varepsilon_s = m_e I_s^2 / (2\hbar^2). \quad (31)$$

As we shall see, the condition  $I_s < 0$  holds for infinitely many possible quantum numbers  $s$  and thus the number of bound states associated with different values of  $s$  is infinite, in accordance with the conclusion

of [1]. For each  $s$ , the estimate (31) gives the binding energy for the state for which the longitudinal part of the wave function of the external electron has no nodes, e.g.  $\nu = 0$ .

To exploit the latter analytical approach let us introduce the transverse probability density for the states related to the ground Landau manifold

$$\rho_s(r_\perp) = \int_0^{2\pi} d\varphi |\langle \mathbf{r}_\perp | n=0, s \rangle|^2 = \frac{1}{s! a_m^2} \left( \frac{r_\perp^2}{2a_m^2} \right)^s \exp \left( -\frac{r_\perp^2}{2a_m^2} \right), \quad (32)$$

where the integration is done over the electron azimuthal angle. In terms of the density (32) and the atomic potential  $V(r_\perp, z)$  we have

$$I_s = \int_0^\infty r_\perp dr_\perp \rho_s(r_\perp) \int_{-\infty}^\infty dz V(r_\perp, z). \quad (33)$$

Let us now adopt an approximation of the atomic potential given by Eq. (19) for large distances. It is easy to check that at any  $r_\perp \neq 0$

$$\int_0^\infty \frac{(2z^2 - r_\perp^2) dz}{(r_\perp^2 + z^2)^{5/2}} = 0 \quad (34)$$

and thus the first, quadrupole, term in (19) does not contribute into  $I_s$ . This implies that the polarization part of the atomic potential plays a key role in binding the external electron. Let us further assume that the influence of the magnetic field on the atomic polarizability is negligible. As it is known [16], in the absence of the magnetic field an atom in the ground state of the zero total angular momentum has an isotropic polarizability,  $\kappa$ , i.e. we assume  $\kappa_\perp \approx \kappa_\parallel \approx \kappa$ . Then the polarization term in (19) is net attractive and the condition  $I_s < 0$  is fulfilled. Straightforward integration in Eq. (33) and use of the relation (31) gives

$$-\varepsilon_s = \frac{\pi^2 \kappa^2}{2^7 (s!)^2} \Gamma^2 \left( s - \frac{1}{2} \right) \text{Ry} \gamma^3, \quad (35)$$

where  $\Gamma$  is the complete gamma-function,  $\text{Ry} = m_e e^4 / (2\hbar^2)$ ,  $\gamma = a_m^2 / a_0^2 = B / B_0$ , and  $B_0 = 2.35 \times 10^5$  T. This estimate is not appropriate for  $s = 0$  because of the divergence of the integrations at the origin  $r_\perp = z = 0$  for the potential (19). However, for  $s > 0$  above value of the binding energy is a good approximation for  $\gamma \ll 1$  (laboratory magnetic fields) since the main contribution to the integral comes from distances sufficiently larger than  $a_0$ , the natural measure of the size of the neutral atom. Using atomic units (2Ry for the energy and  $B_0$  for the magnetic field strength) we rewrite Eq. (35) in a recurrent way,

$$-\varepsilon_s = 0.1211 \kappa^2 B^3 \delta_s^2, \quad s = 1, 2, \dots, \quad (36)$$

where

$$\begin{aligned} \delta_1 &= 1, \\ \delta_s &= [1 - (1.5/s)] \delta_{s-1}, \quad s = 2, 3, \dots. \end{aligned} \quad (37)$$

One should notice that the scaling behaviour of the binding energies with the magnetic field strength,  $-\varepsilon_s \propto B^3$ , coincides with that predicted in [1]. Also, at large  $s$  we have  $\delta_s \approx s^{-3/2}$  and thus obtain the behaviour of the binding energies for large  $s$ ,  $-\varepsilon_s \propto s^{-3}$ . Such a sharp decrease of the binding energy with the quantum number reflects the fact that in the plane perpendicular to the magnetic field the external

electron follows the Landau orbit with the expectation value for the radius squared  $\langle r_\perp^2 \rangle = 2(s+1)a_m^2$ , and at large  $s$  the transverse probability density (32) becomes a peaked function of  $r_\perp^2$  centered around  $r_\perp^2 = \langle r_\perp^2 \rangle$ . Therefore, as  $s$  increases the external electron is bound to the atom at progressively larger distances from it.

We can also establish the behaviour of the binding energy with the magnetic field strength for the state  $s = 0$ . In this case, contrary to the limit of large  $s$ , the transverse probability density varies very slowly with  $r_\perp$  and the scale on which it reduces significantly from its maximal value at  $r_\perp = 0$  is the magnetic length,  $a_m$ , which strongly exceeds the atomic potential scale,  $a_0$ . Therefore, when calculating the integral (33) we can replace the transverse probability density by its maximal value,  $\rho_s(0) = 1/a_m^2$ . In this way we obtain

$$-\varepsilon_0 = \frac{1}{2} \left[ \int_0^\infty r_\perp dr_\perp \int_{-\infty}^{+\infty} dz V(r_\perp, z) \right]^2 B^2 , \quad (38)$$

where we have used atomic units again as in the remaining part of our work. We remark that the domain of the neutral atomic core contributes quite significantly to the integrations in (38) and thus the use of the quasimolecular (adiabatic) picture to describe the motion of the extra electron becomes a crude approximation. However, a more accurate treatment is expected to change only the numerical coefficient in Eq. (38). The scaling behaviour of the binding energy with respect to the field strength is expected to be the same, i.e.  $-\varepsilon_0 \propto B^2$ .

### III. BINDING ENERGIES OF THE H<sup>-</sup> AND H <sub>$\mu$</sub> <sup>-</sup> IONS

The approach developed in the previous Section can be directly applied to the H<sup>-</sup>-ion. With a good accuracy we can neglect the influence of the magnetic field on the ground state of the core electron, and use the well-known value (see, e.g., [17]),  $\kappa = 9/2$ , for the polarizability of such a configuration. Then the estimate (36) gives

$$-\varepsilon_s = 2.453 B^3 \delta_s^2 . \quad (39)$$

More reliable results for the binding energies for the states of the electron attached to the hydrogen atom which are induced by the presence of the magnetic field, including the state  $s = 0$ , can be obtained if one knows the atomic potential  $V$ . When the influence of the magnetic field on the hydrogen atom is neglected this potential is spherically symmetric,  $V = V(r)$ , and can be found in the literature. We use the results of Walles, Herman and Milnes [18] who rigorously calculated the energy levels of an electron moving in the field of two fixed, at distance  $r$  from each other, charges  $+e$  and  $-e$  using the separability of the problem in confocal elliptic coordinates. Their electronic ground state energy,  $E_{\text{WHM}}$ , is directly related to our potential  $V(r)$ ,

$$V(r) = E_{\text{WHM}}(r) - \frac{1}{r} + 0.5 , \quad (40)$$

when adding the Coulomb interaction energy between the two static charges and the hydrogenic ground-state binding energy (cf. Eq. (13)). The energy  $E_{\text{WHM}}$  was tabulated in the wide range of  $r$ ,  $0.840380 < r < 30.0$ . In Figure 1, we show the corresponding values of  $V$  by dots and use the spline interpolation to determine the value of the potential between them (solid line). At larger  $r$  the potential can be evaluated by its polarization tail,

$$V(r) = -\frac{2.25}{r^4}, \quad (41)$$

while at the lower  $r$  one can put  $E_{\text{WHM}} = 0$  in Eq. (40) and get

$$V(r) = -\frac{1}{r} + 0.5. \quad (42)$$

As Figure 1 demonstrates, these extrapolations match very good the data from [18].

With the well-defined potential  $V(r)$  we can find the value of the coefficient in the estimate of the binding energy for the state  $s = 0$ . Numerical integration of the potential in Eq. (38), with the natural replacement  $2\pi r_{\perp} dr_{\perp} dz \rightarrow 4\pi r^2 dr$ , yields

$$-\varepsilon_0 = 6.31B^2. \quad (43)$$

To verify the estimates (39) and (43) we have also solved numerically the Schrödinger equation (28), calculating the effective potentials  $V_s(z)$  numerically from the potential  $V(r)$  presented in Figure 1. First of all, we were searching for the states with no nodes of the longitudinal wave function of the external electron ( $\nu = 0$ -states). The results for the corresponding binding energies, for different numbers of  $s$  and field strengths, are shown in Figure 2 by open circles. Solid lines represent the estimates (39) and (43), and we can conclude that they are in fairly good agreement with the numerical results. We have also performed the search for the bound states with higher longitudinal excitations,  $\nu = 1, 2, \dots$ , but found no one, for the magnetic field strengths  $10^{-6} < B < 10^{-4}$ . This indicates that the effective potential  $V_s(z)$  is so weak that for each  $s$  it can bind the external electron only in the  $\nu = 0$ -state.

Finally, to control the validity of the quasimolecular approach, we have calculated the quantity  $h(r) = h_{00}(r)$ , the non-adiabatic correction to the potential  $V(r)$ , determined by Eq. (10). For this purpose, the wave functions of the electron moving in the field of two fixed charges were computed via a numerical two-dimensional grid method which was invented by M.V. Ivanov (for details of the method as well as the description of the corresponding code ATMOLMESH we refer the reader to [19]). The corresponding results are shown in Figure 1 by open circles. To confirm that the numerical results reproduce correctly the scaling behaviour of  $h$  with  $r$ , we also give the perturbation estimate,

$$h(r) = \frac{8}{r^6}, \quad (44)$$

whose derivation is outlined in the Appendix. With increasing distances exceeding the size of the neutral hydrogen atom, the non-adiabatic correction becomes smaller and smaller compared to  $|V(r)|$ . One should notice that at small  $r$  the non-adiabatic correction exceeds the value of  $|V(r)|$ . This implies that the non-adiabatic coupling effects are quite significant for the state  $s = 0$ . However, since the corresponding binding energy obtained neglecting these effects is very small, we believe that a more accurate approach would only change the numerical coefficient in Eq. (43) but not the scaling low,  $-\varepsilon_0 \propto B^2$ .

The approach developed in this paper can also be directly applied to the analysis of highly excited exotic anions, for example to the ion formed by attaching the muon to the hydrogen atom. Due to the fact that the shell of the  $H\mu^-$ -ion is formed by two different particles (the electron and muon) there is no need for antisymmetrization (exchange) and the ansatz (7) for the wave function of the ion becomes exact. Moreover, since the muon is much heavier than the electron (the muon-to-electron mass ratio is  $m_{\mu}/m_e \approx 207$ ), the binding energies for the muonic ion are larger. Replacement of the electron mass by the muon mass in Eq. (31) leads to the following estimates

$$\begin{aligned} -\varepsilon_0 &= 1306B^2, \quad s = 0, \\ -\varepsilon_s &= 508B^3\delta_s^2, \quad s = 1, 2, \dots . \end{aligned} \tag{45}$$

In Figure 2, the corresponding energies are plotted as dashed lines. Evidently, the non-adiabatic correction to the one-particle potential for the  $H\mu^-$  ion is  $m_\mu/m_e$  times smaller than that for the ion  $H^-$  (see Figure 1), which makes the estimate for  $s = 0$  more reliable in the case of the  $H\mu^-$  ion.

#### IV. SUMMARY AND OUTLOOK

In this paper, we have studied the states of the negative atomic ions which are induced by the presence of a magnetic field. Apart from the neglect of the exchange interaction between the external and atomic (core) electrons the equations we start with are exact. Performing an analysis of the weakly bound states of the external electron, it is possible to reduce the problem to an effective one-particle by neglecting the non-adiabatic coupling terms. In the presence of the magnetic field which determines the transverse motion of the external electron further simplifications are possible which reduce the question of the binding mechanism to a one-dimensional Schrödinger equation for the motion of the external electron along the field.

We can conclude that in the approximation of the infinitely heavy nucleus the number of the ionic bound states is infinite, in accordance with the general theorem of [1]. A quite simple and appealing physical picture of the appearance of such states is that the external electron can be attached to the atom with different values of its angular momentum along the magnetic field. The number of such possible definite values is infinite and for each value a different 1D effective potential appears. This potential determines the motion of the external electron along the field and can bind the electron in at least one quantum state. We have labelled these states by the integer number  $s = 0, 1, 2, \dots$  (negative of the magnetic quantum number of the external electron), and obtained general estimates of the binding energies of negatively charged ions. These estimates establish both the dependence of the binding energies on the magnetic field strength and on the quantum number  $s$ : for  $s = 0$  the binding energy scales with  $B$  as  $B^2$  and for  $s = 1, 2, \dots$  the scaling law is  $-\varepsilon_s \propto B^3$ ; at large  $s$  the binding energies behave as  $-\varepsilon_s \propto s^{-3}$ . To apply the estimates for  $s > 0$  to a specific ion one needs only to know the polarizability of the corresponding neutral atom in an external electric field, while the estimate for  $s = 0$  involves the whole atomic potential acting on a static external electron.

We have applied the estimates obtained to the  $H^-$ -ion, exploiting the known polarizability of the hydrogen atom and the potential for the static two-charge Coulomb problem [18]. We also have verified that these estimates are in complete agreement with results of the numerical integration of the Schrödinger equation for the motion of the external electron along the magnetic field.

The binding energies for the  $H^-$ -ion that we have obtained are indeed very small compared to the binding energy of the hydrogen atom. At the largest magnetic fields available at laboratories now,  $B \sim 30$  T, the binding energy for the  $H^-$ -ion is approximately  $2.8 \times 10^{-3}$  meV for the state with the zero angular momentum of the external electron, and it is  $\approx 1.4 \times 10^{-7}$  meV for the state with  $s = 1$ . The magnetically induced bound states of the exotic muon ions possess a much larger binding energy. For the same value of the magnetic field strength, the muon affinity to the hydrogen atom is 0.58 meV for the state  $s = 0$  and  $2.9 \times 10^{-5}$  meV for the state  $s = 1$ .

It also looks quite challenging to detect the excited anion states for heavier atoms which have polarizabilities significantly larger than the hydrogen atom. For example, the polarizability of Cs is, with 2%

accuracy,  $\kappa = 403$  [17]. The resulting electron affinity to this atom for the state  $s = 1$  at  $B = 30$  T is  $\approx 2 \times 10^{-4}$  meV. Another challenging example is the anion of Ba, which does not exist at  $B = 0$ . The polarizability of Ba, with 8% accuracy, is  $\kappa = 268$  [17], and the binding energy of its excited anion, for the external electron state with  $s = 1$  at  $B = 30$  T is  $\approx 1.8 \times 10^{-5}$  meV. The corresponding states of the exotic ions,  $\text{Cs}\mu^-$  and  $\text{Ba}\mu^-$ , possess the binding energies of  $\approx 4 \times 10^{-2}$  meV and  $\approx 4 \times 10^{-3}$  meV, respectively.

Although we cannot directly apply the estimate (38) for the binding energy of the external electron with zero angular momentum to heavier ions, in order to have an idea about their order of magnitude we can speculate that these binding energies differ from the result (43) by the factor of  $(\kappa/4.5)^2$ , where  $\kappa$  is the polarizability of an atom and 4.5 is the numerical value of the polarizability of the hydrogen atom. In this way we can evaluate the binding energy for the state  $s = 0$  of the external electron of the ion of  $\text{Cs}^-$ , at  $B = 30$  T, as  $-\varepsilon_0 \sim 20$  meV. For the same state of the ion of  $\text{Ba}^-$  we obtain, at the same field strength,  $-\varepsilon_0 \sim 10$  meV. As we see, the magnetically induced anion bound states for atoms with large polarizabilities can very well be detectable in laboratories.

Because of the large extension of the wave function of the loosely bound electron our results may also apply to molecules and clusters although in a less quantitative manner. As molecules and clusters can exhibit large polarizabilities [17] we expect that magnetically induced bound states exist for them and possess considerable binding energies.

One important issue which was not addressed in this paper are the finite nucleus mass effects which can affect the ion states significantly. The underlying physical picture of the finite nuclear motion for charged systems was discussed in detail in, e.g., [20]. Here we only mention that the electron states are affected by an oscillating electric field introduced in the internal (electronic) system of the ion due to the rotation of the ion as a whole over a Landau-like orbit. For a crude estimate, we may assume that due to the ion motion the ion's states get the oscillator-like energy excess  $\hbar\Omega N$ , where  $\Omega = eB/(Mc)$ ,  $M$  is the ion mass and  $N = 0, 1, 2, \dots$ . Since in the presence of the magnetic field the internal (electronic) degrees of freedom are inherently coupled to the center of mass ones [20], we can expect that similar to the case of the positive  $\text{He}^+$ -ion [21] the minimal possible value of  $N$  for stable states coincides with  $s$ . In this case, an  $s$ -state of the external electron is still bound if  $-\varepsilon_s > \hbar\Omega s$ , or

$$\frac{B}{1 \text{ T}} > \frac{1.58 \times 10^4}{A^{1/2}\kappa} \frac{s^{1/2}}{\delta_s}, \quad (46)$$

where  $A$  is the mass number of the ion. According to this criterion, for the  $\text{H}^-$ -ion the magnetic field strength which stabilizes the state  $s = 1$  against the motional Stark effect, is large,  $B \approx 3.5 \times 10^3$  T, and cannot be achieved in laboratories. However, for heavier ions, the magnetic field which can stabilize them in excited states are smaller. For example, for the  $\text{Cs}^-$ -ion, such a field is  $\approx 3.4s^{1/2}\delta_s^{-1}$  T, so the external electron can be bound in a few  $s$ -states at the magnetic fields available at laboratories. We must remark that these estimates of the center of mass effects on the ion bound states are very preliminary and based on the intuitive picture of the inclusion of the oscillator-like energies associated with the ion motion across the magnetic field in the total energy spectrum. We plan to perform the corresponding analysis accurately in order to see how the nuclear motion influences the induced bound states in the magnetic field. But already now we can speculate that the finite nuclear mass effects make at least the highly excited  $s$ -states unbound which means that in reality the actual number of bound ion states is finite and not infinite.

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### Appendix

According to Eq. (10), the non-adiabatic correction to the potential of interaction between the hydrogen atom and an extra electron reads

$$h_{00}(\mathbf{r}) = \frac{\hbar^2}{2m_e} \int d\mathbf{r}_1 \left| \frac{\partial}{\partial \mathbf{r}} \phi_0(\mathbf{r}_1, \mathbf{r}) \right|^2 . \quad (\text{A1})$$

Here integration is performed over the position  $\mathbf{r}_1$  of the core electron and the wave function  $\phi_0$  describes the ground state of the atom perturbed by the interaction with the static external electron. When the interaction is weak, this wave function can be evaluated by the first order perturbation theory,

$$\phi_0(\mathbf{r}_1, \mathbf{r}) = \phi_0^{(0)}(\mathbf{r}_1) + \sum_{f \neq 0} \frac{W_{f0}(\mathbf{r})}{E_0^{(0)} - E_f^{(0)}} \phi_f^{(0)}(\mathbf{r}_1) , \quad (\text{A2})$$

where  $\phi_0^{(0)}$  and  $\phi_f^{(0)}$  are the wave functions of the ground and excited states of the non-perturbed atom, respectively,  $E_0^{(0)}$  and  $E_f^{(0)}$  are the corresponding eigenenergies and

$$W_{f0}(\mathbf{r}) = \langle \phi_f^{(0)} | W(\mathbf{r}_1, \mathbf{r}) | \phi_0^{(0)} \rangle \quad (\text{A3})$$

are the matrix elements of the perturbation operator

$$W(\mathbf{r}_1, \mathbf{r}) = \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}|} - \frac{e^2}{r} . \quad (\text{A4})$$

Substituting (A2) into (A1) and integrating over  $\mathbf{r}_1$  yields, due to the orthogonality of the hydrogenic wave functions,

$$h_{00} = \frac{\hbar^2}{2m_e} \sum_{f \neq 0} \frac{|S_{f0}|^2}{\left( E_0^{(0)} - E_f^{(0)} \right)^2} , \quad (\text{A5})$$

where  $S = \partial W / \partial \mathbf{r}$ . To simplify the latter expression, let us approximate the energy difference in the denominator by the quantity  $-Ry$ . Then, using the completeness property of the hydrogenic wave functions, we obtain

$$h_{00} = \frac{\hbar^2}{2m_e Ry^2} \left[ (S^2)_{00} - (S_{00})^2 \right] , \quad (\text{A6})$$

where  $(S^2)_{00}$  and  $S_{00}$  are the mean values of the operators  $S^2$  and  $S$ , respectively, for the ground state of the non-perturbed hydrogen atom. To calculate them, it is most convenient to specify the internal atomic coordinates with the quantization axis along  $\mathbf{r}$ . In these coordinates, assuming  $r \gg r_1$ , we can replace the operator (A4) by the first, dipole, term of its multipole expansion (cf. Eq (15)),  $W = (e^2/r^2)z_1$ . Then we have  $S = -(2e^2/r^3)z_1$ . For the latter operator, because of the  $z$ -parity of the hydrogenic state, one has  $S_{00} = 0$  and Eq. (A6) reduces to

$$h_{00} = \frac{2\hbar^2 e^4 (z_1^2)_{00}}{m_e \text{Ry}^2 r^6}. \quad (\text{A7})$$

Substituting there the known value  $(z_1^2)_{00} = a_0^2$  and introducing atomic units, we obtain the estimate of the non-adiabatic correction given by Eq. (44),  $h_{00}(r) = 8/r^6$ .

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### Figure Captions

**Figure 1.** The one-particle potential of interaction between the static charge  $-e$  and the hydrogen atom (solid line) and the non-adiabatic correction to this potential for the cases when the charge is associated with the electron (long-dashed line) and with the muon (shot-dashed line). Dots show the reference data for the potential obtained from [18]. The part of the solid line connecting the dots is obtained by the spline interpolation, at lower  $r$  the solid line corresponds to Eq. (42) while at large  $r$  it corresponds to Eq. (41). Open circles show the non-adiabatic corrections obtained numerically, and dashed lines correspond to the perturbation estimates.

**Figure 2.** Binding energies for the states  $s = 0, 1, 2, 3, 4$  (in meV) as functions of the magnetic field strength (in Tesla). The conversion rate used is: 1 a.u. =  $2.35 \times 10^5$  T. Solid lines show the estimates for the ion  $H^-$  given by Eqs. (43) and (39), and dots represent the results of our numerical treatment. Dashed lines show the corresponding energies for the muonic ion,  $H\mu^-$ .



